

DOT/FAA/AR-02/53

Office of Aviation Research
Washington, D.C. 20591

Fire-Resistant Cyanate Ester- Epoxy Blends

May 2002

Final Report

This document is available to the U.S. public
through the National Technical Information
Service (NTIS), Springfield, Virginia 22161.



U.S. Department of Transportation
Federal Aviation Administration

20020805 071

NOTICE

This document is disseminated under the sponsorship of the U.S. Department of Transportation in the interest of information exchange. The United States Government assumes no liability for the contents or use thereof. The United States Government does not endorse products or manufacturers. Trade or manufacturer's names appear herein solely because they are considered essential to the objective of this report. This document does not constitute FAA certification policy. Consult your local FAA aircraft certification office as to its use.

This report is available at the Federal Aviation Administration William J. Hughes Technical Center's Full-Text Technical Reports page:
actlibrary.tc.faa.gov in Adobe Acrobat portable document form (PDF).

1. Report No. DOT/FAA/AR-02/53		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle FIRE-RESISTANT CYANATE ESTER-EPOXY BLENDS				5. Report Date May 2002	
				6. Performing Organization Code	
7. Author(s) Richard N. Walters				8. Performing Organization Report No.	
9. Performing Organization Name and Address Galaxy Scientific Corporation 2500 English Creek Avenue, Building C Egg Harbor Township, NJ 08234				10. Work Unit No. (TRAIS)	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Aviation Research Washington, DC 20591				13. Type of Report and Period Covered Final Report	
				14. Sponsoring Agency Code AIR-120	
15. Supplementary Notes The FAA William J. Hughes Technical Center COTR is Richard Lyon.					
16. Abstract The cure chemistry, thermal stability, and fire behavior in a series of fire-resistant cyanate ester-epoxy blends were examined. The dicyanate and diepoxide of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol-C, BPC) were combined in various molar ratios, and the reaction chemistry was monitored using Fourier Transform Infrared Spectroscopy (FTIR) and differential scanning calorimetry (DSC). Fire behavior of the BPC cyanate-epoxy blends was studied in flaming and nonflaming combustion, using fire calorimetry and pyrolysis-combustion flow calorimetry, respectively.					
17. Key Words Cyanate ester, Epoxy, Fire, Thermal analysis, Calorimetry				18. Distribution Statement This document is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 20	
				22. Price	

ACKNOWLEDGEMENT

The author would like to thank Ciba Performance Polymers and Pacific Epoxy Polymers for supplying the cyanate ester and epoxy resins used in this study.

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	vii
INTRODUCTION	1
EXPERIMENTAL	1
Materials	1
Sample Preparation	2
Differential Scanning Calorimetry	2
Infrared Spectroscopy	2
Thermal Gravimetric Analysis	3
Rheology	3
Microcalorimetry	3
Composite Panel Preparation	3
Fire Calorimetry	4
RESULTS AND DISCUSSION	4
Differential Scanning Calorimetry	4
Infrared Spectroscopy	5
Thermal Gravimetric Analysis	7
Rheology	9
Microcalorimetry	9
Fire Calorimetry	10
CONCLUSION	11
REFERENCES	12

LIST OF FIGURES

Figure		Page
1	DSC Curves for Blended BPC Resins Heated at 1°C/min Under Nitrogen	5
2	IR Spectra of Uncured and Cured 6:4 Blend of the Cyanate Ester and Epoxy	6
3	Normalized Infrared Peak Heights for the Reactants and Products of the 6:4 Cyanate Ester-Epoxy Blend	7
4	Cyclotrimerization Reaction of the Cyanate Ester (A) and the Subsequent Reaction With Glycidylether (B) to Form the Oxazoline	7
5	TGA Traces for the Neat and Blended BPC Resins Heated at 10°C/min Under Nitrogen	8
6	PCFC Heat Release Rates for the Series of BPC Resins	9
7	Heat Release Rate Curves From the OSU Calorimeter	11

LIST OF TABLES

Table		Page
1	Thermal Analysis Results From DSC, TGA, and Rheometer	5
2	Flammability Results From PCFC and OSU for BPC Polymers and Reference Materials	10

EXECUTIVE SUMMARY

The cure chemistry, thermal stability, and fire behavior in a series of fire-resistant cyanate ester-epoxy blends were examined. The dicyanate and diepoxide of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol-C, BPC) were combined in various molar ratios and the reaction chemistry was monitored using Fourier Transform Infrared Spectroscopy (FTIR) and differential scanning calorimetry (DSC). Fire behavior of the BPC cyanate-epoxy blends was studied in flaming and nonflaming combustion, using fire calorimetry and pyrolysis-combustion flow calorimetry (PCFC), respectively.

INTRODUCTION

A chlorine-containing bisphenol, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol-C, BPC), is being studied by researchers at the Federal Aviation Administration (FAA). Bisphenol-A (BPA) is used in the synthesis of several different polymers for which bisphenol-C (BPC) can be substituted. Some of these polymers include thermoplastics, such as polycarbonate and polyester, and thermosetting resins, such as cyanate esters and epoxies. Polymers derived from BPC show similar thermal, mechanical and processing properties as in BPA containing polymers but with considerably reduced flammability [1-3]. This is desirable because almost no changes have to be made in the processing routine or equipment for manufacturing parts with improved flammability resistance. In a previous study [2], a reduction in the flammability was demonstrated using oxygen index (LOI) and a vertical Bunsen burner test (UL-94) for several BPA and BPC epoxy systems. Other desirable flammability properties that were effected were an increase in the char yield and a reduction in the peak and total heat release rates. The previous study was conducted to demonstrate the reduction in heat release without modification by fillers or additives. One of the objects of this study is to reduce the flammability of the BPC epoxy (BPCE) further by reacting it with the less flammable BPC cyanate ester (BPCCE) [4]. Blending the resins allows for modification of properties such as glass transition temperature, mechanical properties, and adhesion while reducing the cost.

Epoxies are well suited for use in aircraft due to their excellent mechanical properties, low cost, and ease of processing. However, the flammability of epoxies excludes them from use in aircraft. Less flammable phenolic resins are now used for the interior panel construction despite their problematic mechanism of cure. Water is a by-product of the condensation reaction which vaporizes in the matrix to reduce the strength and surface smoothness on the panels. Panels made with cyanate ester-epoxy systems may have a better surface finish at comparable or better heat release.

The chemistry of the BPA cyanate ester-epoxy systems has been examined and documented [5-10]. Several reactions occur in the systems that are being evaluated. Upon heating, several cyanate ester functional groups will undergo a cyclotrimerization reaction to form a triazine linkage [11-13]. The epoxide functionality also reacts with other epoxide groups to form a polyether. Also, the epoxide reacts with the triazine to form a five-membered oxazoline ring [6 and 10]. Each of these reactions occurs in varying amounts depending on the ratio of the blend. Evidence supporting these reactions will be discussed.

EXPERIMENTAL

MATERIALS.

All materials were used as received from the manufacturers without modification. The BPC cyanate ester (trade name: RD 98-228) was received from Ciba Performance Polymers. The BPC epoxy (XPR-1015) was received from Pacific Epoxy Polymers and had a reported equivalent weight of 209.3 g/eq. In this report the blended resins are referred to by the molar formulation of the cyanate ester to the epoxy. All gases used for the instrumentation/experimentation were ultra-high purity (UHP) grade and were supplied by Welco Gases.

SAMPLE PREPARATION.

Blended samples of the cyanate ester and epoxy were prepared in ratios ranging from 0 to 100 mole percent. The initial screening required a small sample blend and only 1 gram of each blend was prepared. The reported functionality of the supplied resins were used to calculate the needed weight of each component for all of the formulations. The resins were supplied as solids and had to be warmed gently to produce a liquid with low viscosity. Melting points were determined experimentally by using differential scanning calorimetry (DSC). Once the resins were melted, they would remain liquid for several days before recrystallizing into a solid. Formulated samples were weighed as solids, heated to the melting temperature, and held there until completely melted. Once the samples were liquid, they were easily mixed and cooled prior to analysis. Blended liquid samples were then used for DSC and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The remaining unreacted resin was then cured for additional analysis. Thermogravimetric analysis (TGA) and pyrolysis-combustion flow calorimetry (PCFC, Microcalorimetry) were used to determine the thermal stability and flammability. Samples were cured in an oven and were sampled periodically to determine the extent of cure. Samples were placed in a convection oven at 100°C for 2 hours and ramped in 50°C increments every 2 hours, to a maximum temperature of 200°C, where they were held for 4 hours. Larger samples including the cyanate ester, cannot be heated fast due to a large exotherm during cure.

DIFFERENTIAL SCANNING CALORIMETRY.

The DSC (Perkin Elmer DSC 7) was used to determine the melting points, T_m , of the neat resins and the heat of reaction, ΔH_{rxn} , for all the resin systems. For the melting point determination, approximately 3 mg of the neat sample was put in an open pan, weighed, and placed in a DSC purged with nitrogen. The samples were then heated from 30°C at 5°C/min until the melting endotherm was observed. The DSC was also used for examining the heat of reaction of the blended resin systems. Approximately 3 mg of sample was placed in an aluminum pan, weighed, and sealed in a press. The sealed pan was then placed inside the DSC and the sample heated at several different heating rates from 100° to 250°C. Two runs were performed on each sample for the determination of the heat of reaction. The first run was for obtaining the heat of reaction. The second was for obtaining a baseline with the same shape and magnitude as the sample run. Heats of reaction were determined by integrating the sample curve after subtracting it from the baseline.

INFRARED SPECTROSCOPY.

The FTIR was used to monitor the extent of reaction and to investigate the cure chemistry. Thin films of the neat and blended resins were cast on salt plates prior to their cure for spectral analysis. The salt plates were then placed in a convection oven and the resins cured slowly. Spectra consisting of 32 scans at a resolution of 2 wave numbers were taken periodically during the cure to monitor the extent of reaction and determine what bands were appearing/disappearing. All of the samples were heated until the bands for the reactants completely disappeared, indicating completion of the cure. Additional sets of experiments were performed in the sample compartment of the FTIR where the resins were cured in a heated transmittance cell. Liquid resin was placed between two salt plates and placed in the heated block assembly of a heated cell (Hot One-CIC Photonics Inc.). The sample was then heated from 100° to 300°C at

2°C/min. Spectra were taken every 2 minutes to obtain complementary data for some of the experiments from the DSC. Several bands were monitored for reactant consumption and product formation in the infrared. The bands for the reactive cyanate ester functionality are located at 2270 cm^{-1} . Bands for the epoxide, located at 915 cm^{-1} and 3000 cm^{-1} , are also clearly visible. The triazine ring has a strong absorbance at 1565 cm^{-1} and the oxazoline has an absorbance at 1608 cm^{-1} . These bands were monitored to determine the extent of cure for all of the samples.

THERMAL GRAVIMETRIC ANALYSIS.

The TGA was used to evaluate the temperature at which the liquid resins started to evaporate and to monitor the thermal stability of the reacted blends. The uncured neat and blended resins were heated at 10°C/min to determine a maximum temperature at which the resins could be cured without losing any reactant due to volatilization. The thermal stability of the reacted resin systems were also examined. Approximately 8 mg of each cured sample was placed in the TGA and heated from 50° to 900°C at 10°C/min under a nitrogen purge. Replicate tests on all samples and daily calibration checks were performed to ensure the validity of the data. Trends correlating with blend formulation ratio were examined.

RHEOLOGY.

A rheometer (Rheometrics RDA2) was used to determine the glass transition temperature, T_g , of the blends. Rectangular test strips measuring 1 cm x 3 cm were cut from single-layer glass laminates, described later, for the analysis. The composite strips were placed in a torsion fixture for the rheometer and tested under oscillatory conditions. Samples were subjected to a dynamic temperature ramp and heated in air at 5°C/min from 30°C until the transition was observed. A frequency of 1 Hz was used with a strain setting of 0.35%.

MICROCALORIMETRY.

A pyrolysis-combustion flow calorimeter [14-16] was used as the first test to screen the materials for flammability. Approximately 1 mg of each cured sample was weighed with a microbalance and placed in a Pyroprobe (CDS Analytical Model 2000) for rapid pyrolysis. The probe was placed into a heated interface continuously purged with pure nitrogen. The sample was then programmed to heat at 5°C/s from below the degradation onset temperature to 1200°C and held there for 30 seconds. During pyrolysis, the volatilized decomposition products are transferred in the stream of nitrogen to a high-temperature combustion furnace where pure oxygen is added and the decomposition products are completely combusted. The amount of oxygen consumed is measured with an oxygen analyzer and used to calculate a heat release rate using Thornton's rule [17-19]. Additional analysis yields the material property heat release capacity, η_c [20].

COMPOSITE PANEL PREPARATION.

Single-ply glass laminates (S-Glass with an 8HS weave and an areal density of 303.4 g/m^2) were prepared for fire calorimetry tests. Individual samples were prepared using a hand layup technique and were cured in a small heated press (Carver Model M). The volume fraction of resin in the resulting composite was controlled by pressing to a predetermined gap setting in the

custom-made, polytetrafluoroethylene-coated plates. The panels prepared had approximately a 40% weight pickup of resin.

FIRE CALORIMETRY.

An Ohio State University (OSU) fire calorimeter was used to evaluate the flammability of the cyanate ester-epoxy blends under standard conditions [21]. The OSU is a bench-scale fire calorimeter that requires a 15- x 15-cm sample which is mounted vertically. After thermal equilibration in a holding chamber, samples are rapidly exposed to a 35 kW/m² heat flux with a pilot flame impinging on the sample surface. The OSU also has a gas burner above the sample which aids in the combustion of the evolved gases. The stock OSU calorimeter determines flammability by measuring the temperature rise of the effluent gas stream which is the convective component of the heat release. The single-ply glass lamina was tested for heat release using the OSU. The neat and blended BPC polymers were tested in addition to several reference materials for comparison, including BPA epoxy, phenolic resin, and a polyvinylidene fluoride (PVDF) decorated phenolic panel. Unfortunately, no BPA cyanate ester resin was available to make a composite panel for comparison in this study. Results from the standard OSU test will be discussed.

RESULTS AND DISCUSSION

DIFFERENTIAL SCANNING CALORIMETRY.

The melting points determined by DSC were 75° ±2°C for the BPCCE and 91° ±4°C for the BPCE. The heats of reaction were also determined by DSC. One peak was obtained for each of the neat resins (not shown or designated in figure 1) and two peaks were obtained for each of the blends as shown in figure 1. The two large exotherms were observed for the BPC blends in the DSC, and infrared spectroscopy was used to assign reactions to the measured heat flow, which will be discussed later. The homopolymers of the BPA and BPC epoxy did not react on their own like the cyanate ester and had to be cured with an imidazole catalyst (2-ethyl-4-methyl imidazole) [22-24]. It was found that the BPC epoxy cured at a much lower temperature, 90°C, whereas the BPA epoxy with the same amount of catalyst did not cure until over 200°C. The peak heat flow temperatures for the two large exotherms and total heats of reaction for the BPC polymers are shown in table 1.

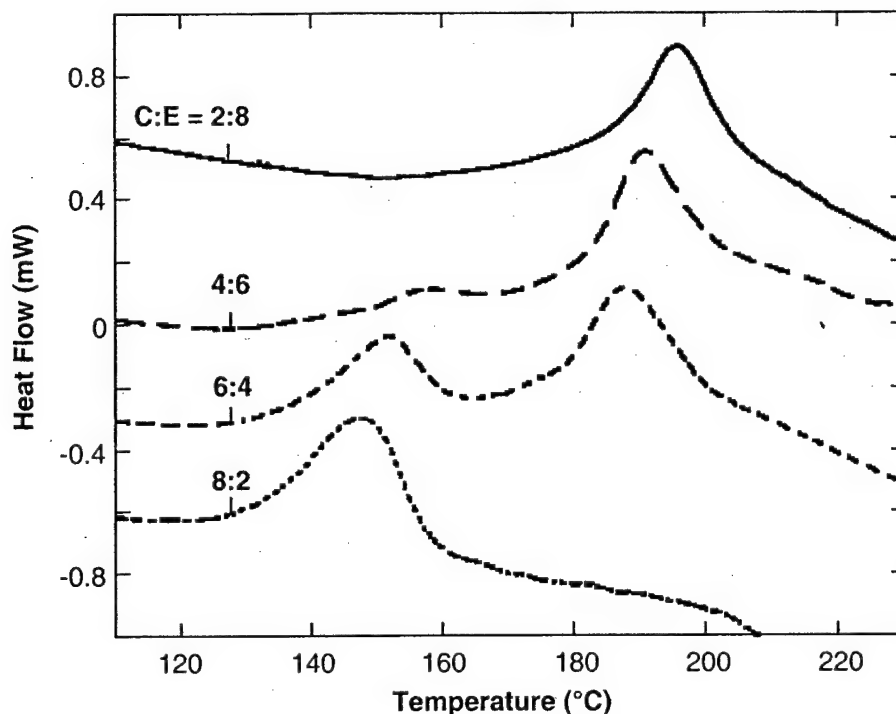


FIGURE 1. DSC CURVES FOR BLENDED BPC RESINS HEATED AT 1°C/min UNDER NITROGEN

TABLE 1. THERMAL ANALYSIS RESULTS FROM DSC, TGA, AND RHEOMETER

Sample	DSC			TGA			Rheometer
	T _C (°C)	T _E (°C)	ΔH _{rxn} (J/g)	Onset (°C)	T _p (°C)	Char Yield (%)	T _g (°C)
BPCCE	198	NA	270	460	479	55.8	247
8:2	147	199	450	335	352	53.9	242
6:4	151	188	612	341	346	52.3	226
4:6	157	191	375	347	350	47	206
2:8	162	196	333	377	381	41.4	153
BPCE	NA	91*	243	360	363	45.5	189

* BPCE was cured with an imidazole catalyst.

INFRARED SPECTROSCOPY.

Figure 2 highlights the bands of interest for the reactants and products. The products being monitored are the cross-linking bonds that are formed by the cyanate ester cyclotrimerizing to form the triazine linkage, the epoxide reacting with another to form a polyether, and the epoxy reacting with the cyanate ester to form the oxazoline linkage.

The reactant and product bands were monitored as a function of temperature for the 6:4 cyanate to epoxy blend in the sample compartment of the FTIR. The samples were heated at 2°C/min to match one of the heating rates used in the DSC. The peak heights were monitored as a function of temperature to analyze the chemistry of the reactions. Figure 3 shows the progress of the reaction. Initially it was thought that the epoxy and cyanate ester reacted with each other to form the oxazoline. The cyanate ester reacts first to form the six-membered triazine ring. This reaction proceeds at a much lower temperature than the neat cyanate ester. This is due to -OH groups formed by the ring opening of the epoxy which catalyzes the cyanate reaction [25 and 26]. Once the triazine is generated, it reacts with the epoxy to form the five-membered oxazoline. The maximum rate of epoxy consumption was observed after almost all of the cyanate ester had been consumed. Work has already been done to determine the mechanism for the reaction. The literature in references 8 and 9 suggested several mechanisms for the cyanate ester-epoxy systems, including a rearrangement within the network structure to form an oxazolidinone. Another mechanism suggests the reaction of the oxirane ring with the triazine to form the oxazoline [6, 7, and 10] as shown in figure 4.

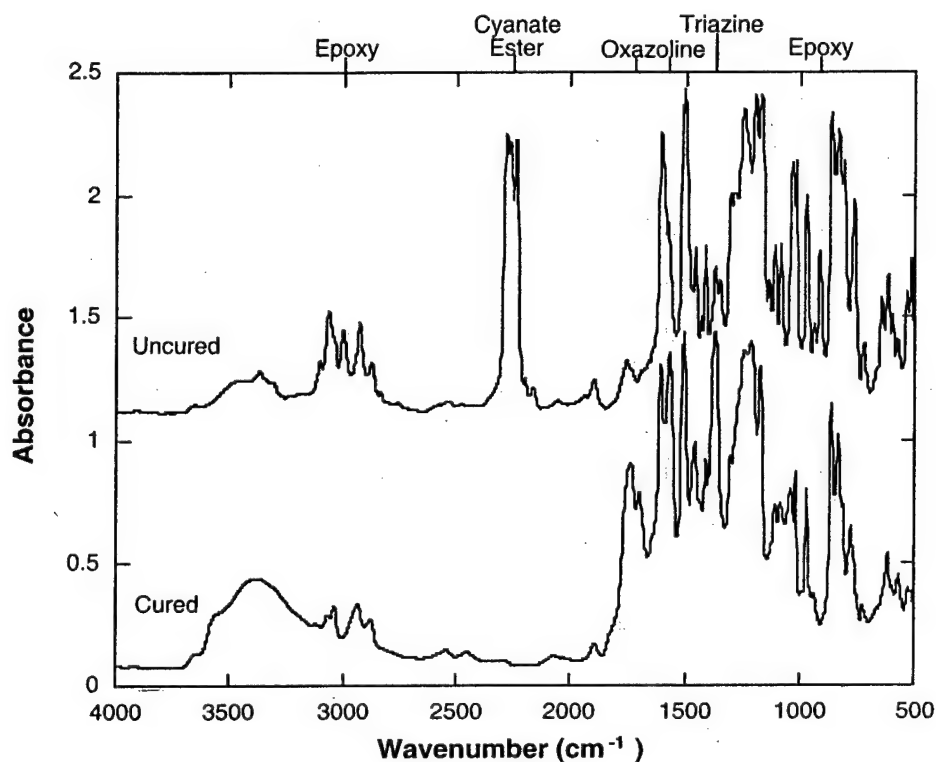


FIGURE 2. IR SPECTRA OF UNCURED AND CURED 6:4 BLEND OF THE CYANATE ESTER AND EPOXY

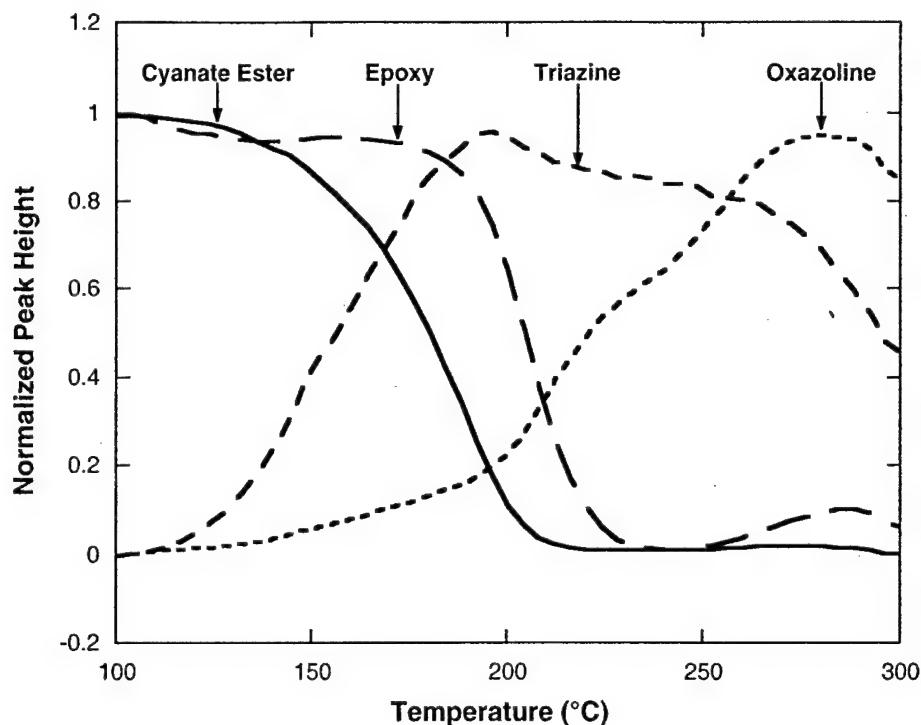


FIGURE 3. NORMALIZED INFRARED PEAK HEIGHTS FOR THE REACTANTS AND PRODUCTS OF THE 6:4 CYANATE ESTER-EPOXY BLEND

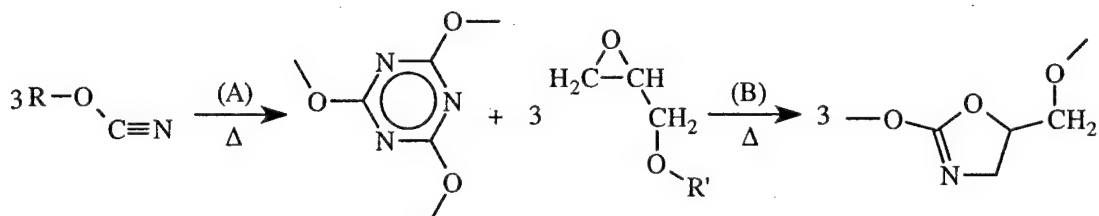


FIGURE 4. CYCLOTRIMERIZATION REACTION OF THE CYANATE ESTER (A) AND THE SUBSEQUENT REACTION WITH GLYCIDYLETHER (B) TO FORM THE OXAZOLINE

THERMAL GRAVIMETRIC ANALYSIS.

The observed mass loss onset temperatures for the liquid BPCCE and BPCE resins were 252° and 299°C, respectively. The weight loss curves for the reacted solid resins are presented in figure 5. It was found that several characteristics of the TGA trace correlated with the molar formulation ratio. A summarization of these trends is presented in table 1. The amount of weight lost in the major decomposition step, as well as the char yield, correlated with the formulation ratio. Values obtained for all blends fell between those from the BPCCE and BPCE, with the exception of the 2:8 blend. A decrease in the onset temperature and an increase in the peak pyrolysis temperature was observed for the 2:8 blend. All of the tests were reproduced to confirm these observations.

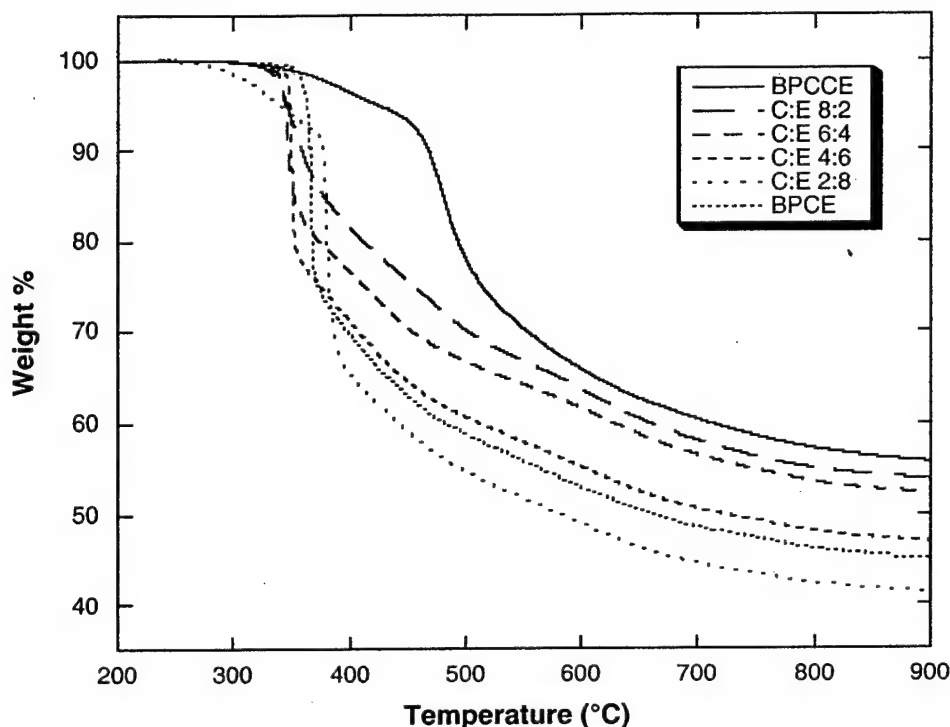


FIGURE 5. TGA TRACES FOR THE NEAT AND BLENDED BPC RESINS
HEATED AT 10°C/min UNDER NITROGEN

The decomposition mechanism and products for a BPC polycarbonate have been identified by Ramirez [3]. He found that the dichloroethylene group, between the two phenyl rings, rearranges to form stilbenes and acetylenes, releasing hydrogen chloride (HCl) as a degradation product at about 400°C. The presence of labile hydrogen as -OH in the BPC epoxy systems lowers the degradation temperature to around 350°C. The decomposition mechanism and products for the triazine ring have been identified by Ramirez and Schimp, respectively [27-29]. In their studies, they found the triazine ring depolymerizes regenerating the -OCN functionality at around 475°C. This is illustrated by the neat BPCCE in figure 5. The neat BPCE and the formulated samples all had the major decomposition step occur around 350°C. It is believed that the oxazoline is degrading first, along with the chlorine abstraction. There is a high weight percent of chlorine (18%-21%) in the BPC polymers. Loss of the chlorine, as HCl, could account for almost all of the weight lost in the major decomposition step. An initial infrared analysis of the gas phase decomposition products from the BPC cyanate ester and epoxy blends under vacuum was performed. The gas phase spectra show ammonium chloride and CO₂ generated early, followed by HCl, phenol, and -OCN in the major decomposition step (~350°C). The presence of CO₂ and ammonium chloride, which has nitrogen and a high concentration of hydrogen, infers the oxazoline as the source of these products. Ammonia, methane, and CO were observed in the gas phase later in the decomposition (>550°C).

RHEOLOGY.

The glass transition temperatures of the blends are presented in table 1. The BPCCE was found to have a T_g of 247°C and the BPCE a T_g of 189°C. The blended resins T_g fell between the two values for the neat resins with the exception of the 2:8 BPCCE:BPCE which was considerably lower.

MICROCALORIMETRY.

Trends in the measured heat release rates (HRR) of the blends were observed. The heat release capacity measured in the nonflaming test show a decrease in the heat release capacity with an increasing cyanate concentration as shown in figure 6. The microcalorimeter results are summarized in table 2. A large reduction in the peak HRR of the BPC epoxy systems was observed with the addition of as little as 20 percent cyanate ester. The peak rate of heat release and the total heat release increase when there is an increase in the epoxy concentration. It is believed that the large aliphatic portion of the epoxy is responsible for the increasing heat release rate. Increasing aromatic group concentration reduces the heat release rate by providing less fuel and more char, typically. The shape of the heat release curves for the BPCCE and the blends were all similar with a sharp peak followed by a low, broad peak, indicating several steps in the decomposition as evidenced by TGA. The neat BPCE had a single, sharp peak which indicates a single-step decomposition. The presence of ammonium chloride in the gas phase IR spectra indicates a large amount of hydrogen which could account for the sharp heat release peak observed in this test.

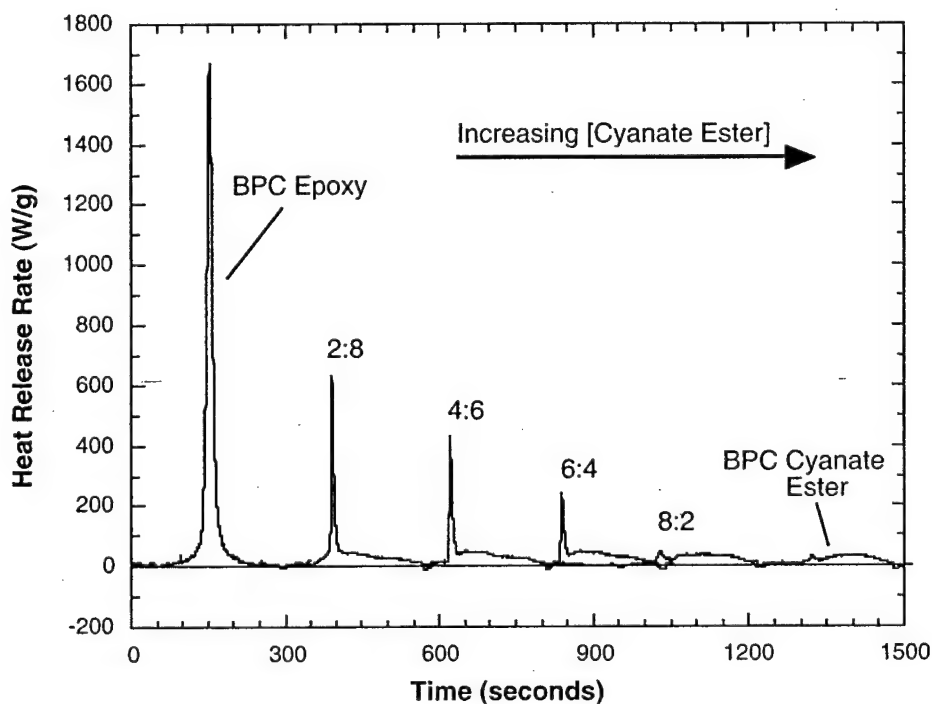


FIGURE 6. PCFC HEAT RELEASE RATES FOR THE SERIES OF BPC RESINS (Shifted in time for clarity)

TABLE 2. FLAMMABILITY RESULTS FROM PCFC AND OSU FOR BPC POLYMERS AND REFERENCE MATERIALS

Sample	PCFC			OSU		
	HR Capacity (J/g-K)	Total Heat Release (kJ/g)	Char Yield (%)	Peak Heat Release (kW/m ²)	2 min Total Heat Release (kW/m ² min)	Char Yield [†] (%)
BPCCE	13	4	59	14	13	27
8:2	13	5	53	18	18	30
6:4	149	6	52	30	15	22
4:6	291	8	42	34	18	16
2:8	393	9	33	32	22	14
BPCE	506	10	36	49	27	14
BPCE	283	18	36	NA	NA	NA
BPAE	657	26	4	110	44	2
Phenolic	NA	NA	NA	23	21	14

† Char yield is based on resin fraction of the composite panel.

FIRE CALORIMETRY.

Definite trends were observed in the flammability behavior of the BPC polymer blends as shown in figure 7. The peak heat release rate and the 2-minute total heat release increased with an increase in epoxy concentration. Only a single test was performed on each of the neat and blended resins due to a limited supply of the BPC resins. The results from the tests are summarized in table 2. All of the materials tested in this study passed the FAA 65/65 flammability requirements [21] for large surface area components with the exception of the BPA epoxy.

The high thermal stability, increased char, and low heat of combustion of the evolved gases contribute to the low flammability of the BPC polymers. The BPC polymers were found to have a high concentration of HCl in the products of combustion. It is well known that halogens poison the flame chemistry by scavenging free radicals. It is also well known that HCl is thermally stable and does not react with oxygen in a combustion reaction and does not contribute to the heat release of the material. The epoxy is more flammable than the cyanate ester due to the increased aliphatic content in the reacted networks. However, there is a considerable reduction in the measured heat release of the BPC epoxy when compared to the BPA epoxy. This demonstrates the effect that substituting one group in the polymer backbone has on the polymer flammability.

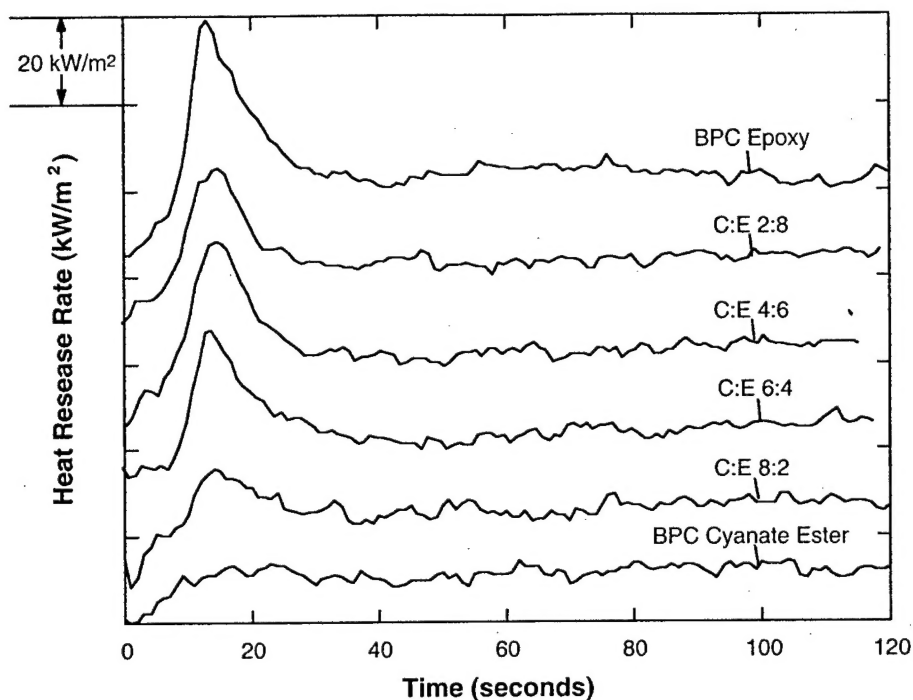


FIGURE 7. HEAT RELEASE RATE CURVES FROM THE OSU CALORIMETER
(The heat release curves have been shifted along the y axis for clarity)

The char yields from the two flammability tests did not correlate well due to the different sample environments. Pyrolysis in the microcalorimeter is completely anaerobic. Conditions in the OSU are only anaerobic at the sample surface when the sample is burning. If the sample does not ignite or ceases to burn, it is subjected to the radiant heat flux and an impinging flame for the duration of the test. The high volumetric flow rate of air sweeping over the sample surface at elevated temperatures causes oxidative pyrolysis and a lower char yield.

Although the heat release rate of the samples with a high epoxy formulation ratio were not as low as was hoped, one must keep in mind that these are unmodified resins that have passed the FAA heat release requirement of a maximum of 65 kW/m^2 peak and 65 kW/m^2 min total. Additives and fillers can be used to optimize the flammability performance as well as other properties such as the glass transition temperature and toughness. These studies are beyond the scope of this report and may be examined in the future.

CONCLUSION

The epoxy and cyanate ester derived from bisphenol-C (BPC) show improved heat release rates relative to their bisphenol-A (BPA) versions. Low fuel content, high char yields, and halogen inclusion in the polymer structure all contribute to the low heat release rate of these materials. The blended resins showed a rule of mixtures increase in the heat release rate with increasing epoxy concentration. These materials show promise as a candidate for inclusion in commercial aircraft. All of the fabricated lamina of the BPC cyanate ester and epoxy had a good surface finish and passed Title 14 Code of Federal Regulations Part 25.853 (a-1).

REFERENCES

1. Katedra, Tworzyw, Sztucznych, Politechnika Warszawska, by Zbigniew K. Brzozowski and Stanislaw Porejko, "Self-Extinguishing Epoxy Resins of Low Viscosity," Polnishes Patent 53,272 (Cl. C 08g), June 28, 1967, Applied, February 24, 1965.
2. R.E. Lyon and L.M. Castelli, "Flammability and Mechanical Properties of a New Fire Resistant Epoxy," 46th International SAMPE Symposium, Long Beach, California, May 6-10, 2001.
3. M.L. Ramirez, "Thermal Degradation Mechanism of Chloral Based Polymers," Masters Thesis, University of Puerto Rico (Mayaguez), January 2000.
4. B. Lin, "Cyanate Esters with Improved Fire Resistance," 44th International SAMPE Symposium, Long Beach, CA, May 23-27, 1999.
5. P. Penczek, B. Szczepaniak, and J. Rejdch, "Synteza Oligomerow Epoksydowo-Oksazolidonowych, Polimery—Tworzywa Wielkocząsteczkowe," 1986.
6. Lonza product brochure, Cyanate Ester Resins—PrimasetTM Resins
7. D.A. Schimp, F.A. Hudock, and S.J. Ising, International SAMPE Symposium, 33, 754 1988.
8. I. Hamerton, Chemistry and Technology of Cyanate Ester Resins, Chapter 3, p. 77, 1994.
9. I. Hamerton, Chemistry and Technology of Cyanate Ester Resins, Chapter. 5, p. 128, 1994.
10. I. Hamerton, Chemistry and Technology of Cyanate Ester Resins, Chapter 6, p. 173, 1994.
11. D.A Schimp, Christenson, J.R., and Ising, S.J., 34th International SAMPE Symposium, 34, 222, 1989.
12. J. Galy, J.F. Gerard, and J.P. Pascault, "Reactivity of Cyanate Ester Resins and Characterization of Polycyanurate Networks, Polyimides and Other High-Temperature Polymers," Elsevier Science Publishers, B.V., Amsterdam, 1991.
13. I. Hamerton, "Chemistry and Technology of Cyanate Ester Resins," Chapter 3, p. 58, 1994.
14. R.E. Lyon and R.N. Walters, "Microscale Combustion Calorimeter," US5981290, November 9, 1999.
15. R.N. Walters and R.E. Lyon, International SAMPE Symposium, 42, 1335, 1997.

16. R.E. Lyon and R.N. Walters, "A Pyrolysis-Combustion Flow Calorimeter Study of Polymer Flammability," Ninth Annual BCC Conference, Stamford, CT, June 1-3, 1998.
17. W.M. Thornton, *Philos. Mag.* 33, 196, 1917.
18. C. Hugget, "Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements," Center for Fire Research, National Bureau of Standards, Washington, DC 20234, *Fire and Materials*, Vol. 4 (2), 1980.
19. R.N. Walters, S.M. Hackett, and R.E. Lyon, "Heats of Combustion of High Temperature Polymers, *Fire and Materials*, 24, 245-252, 2000.
20. R.E. Lyon and R.N. Walters, "Heat Release Capacity," *Fire and Materials* 7th International Conference and Exhibition, January 22-24, 2001.
21. FAR 25.853, "Heat Release Test for Cabin Materials," Aircraft Materials Fire Test Handbook, DOT/FAA/AR-00/12, 2000.
22. J. Vogt, "Thermoset Matrices for Structural Adhesives," *J. Adhesion*, Vol. 22, pp. 139-151, 1987.
23. F. Ricciardi, W.A. Romanchick, and M.M. Joullie, "Mechanism of Imidazole Catalysis in the Curing of Epoxy Resins," *Journal of Polymer Science*, Vol. 21, pp. 1475-1490, John Wiley & Sons, Inc., 1983.
24. V. Jisova, "Curing Mechanism of Epoxides by Imidazoles," *Journal of Applied Polymer Science*, Vol. 34, pp. 2547-2558, John Wiley & Sons, Inc., 1987.
25. A. Osei-Owusu and G.C. Martin, "Analysis of the Curing Behavior of Cyanate Ester Systems," *Polymer Engineering and Science*, Vol. 31, No. 22, 1991.
26. A. Osei-Owusu and G.C. Martin, "Catalysis and Kinetics of Cyclotrimerization of Cyanate Ester Resin Systems," *Polymer Engineering and Science*, Vol. 32, No. 8, 1992.
27. M.L. Ramirez, R.N. Walters, E.P. Savitski, and R.E. Lyon, "Thermal Decomposition of Cyanate Ester Resins," Manuscript in progress.
28. R.E. Lyon, R.N. Walters, and S. Gandhi, "Combustibility of Cyanate Ester Resins," 43rd International SAMPE Symposium, Anaheim, California, May 31-June 4, 1998.
29. D.A. Schimp and S.J. Ising, American Chemical Society National Meeting PMSE Division, April 1992, San Francisco, California, ACS Press, Washington D.C., 1992.